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# RPPR Final Report

## as of 19-Apr-2018

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**Final Report** for Period Beginning 15-Apr-2016 and Ending 14-Apr-2017

**Title:** Mechanisms for Catalytically Abating Organosulfur Compounds with H<sub>2</sub>O<sub>2</sub> Formed In Situ

**Begin Performance Period:** 15-Apr-2016

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**STEM Degrees:** 0

**STEM Participants:** 5

### Major Goals: Monofunctional Catalyst Research Activity:

Task 1) We will synthesize a variety of supported metal-oxide catalysts (e.g., V, Nb, Ta) to study the formation and reaction of M<sup>+</sup>-OOH\* moieties with organic reactants to determine the rates, selectivity, and mechanism for small-molecule oxidation. We will synthesize a series of similarly structured metal-oxide catalysts by depositing low-loadings (0.2 - 3 % wt.) of V, Nb, Ta, Ti, etc. precursors onto silica by SEA and into zeolite frameworks by treating zeolite with moderate aluminum content (e.g., Si/Al ~ 25) with strong HNO<sub>3</sub> solutions followed by metal-ion exchange.

Task 2) Following thermal treatments, we will confirm that added metals are isolated on silica and in frameworks using: 1) ICP to confirm metal content in the catalyst, 2) UV-Visible spectroscopy, because metal atoms in framework positions show a much greater band gap (i.e., absorption edge at lower wavelengths) than seen for nanometer sized agglomerations, and 3) powder X-ray diffraction to confirm incorporation into zeolite frameworks.

Task 3) We will compare the turnover rates and the selectivities for oxidations of alkenes and thiophenes by H<sub>2</sub>O<sub>2</sub> on these catalysts to determine if the Pauling electronegativity of the active metal centers is a useful descriptor for rates, as seen for alkenes. At the start, we will investigate olefin epoxidation to probe metal oxide reactivity as olefins are safer to handle, and we believe the trends in reactivity can easily be extended to thiophenes and related electron-rich molecules.

Task 4) We will conduct oxidation experiments using a series model molecules (e.g., cyclohexene, 2,3-dimethyl but-2-ene, 1-hexene) in well-mixed batch reactors using external H<sub>2</sub>O<sub>2</sub>. By varying the type of reactant used, we can study how alkyl substitution affects oxidation selectivities and reactivities for specific parts of a molecule. These experiments will provide quantitative values for turnover rates and H<sub>2</sub>O<sub>2</sub> selectivities as a function of olefin substitution. Results obtained from olefin epoxidation will then be extended to substituted-thiophenes to guide catalyst design for oxidation with H<sub>2</sub>O<sub>2</sub>.

Task 5) We will also use in situ vibrational spectroscopy to characterize active surface intermediates. The compositions and local environments of catalytic metal-oxide clusters determine, in part, oxidation selectivities. The critical intermediates of interest (e.g., M<sup>+</sup>-OOH\*, thiophenes and sulfones) possess vibrational signatures that are easily observable by FTIR. By monitoring the intermediates formed in situ, we can begin to understand how the intrinsic elemental properties of the different metal-oxide catalysts affect their propensity for oxidation with H<sub>2</sub>O<sub>2</sub>. For example, there may be multiple reactive intermediates (i.e., metal- peroxo, hydroperoxo, superoxo, etc.) that are present in varying proportions depending on the reaction conditions, each of which may be selective for reaction with a specific type of olefin.

Investigate the Chemical Communication between Catalytic Functions

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### Multifunctional Catalyst Research Activities:

We will develop tandem catalytic systems leveraging the in situ production of H<sub>2</sub>O<sub>2</sub> from Pd-based catalysts with the metal-oxide-based oxidation catalysts described previously. We will study the network of reactions that occur when we combine a H<sub>2</sub>O<sub>2</sub> formation catalyst and a high-surface area Lewis acidic oxide catalyst. A critical part of the investigation is to determine how these “tandem” catalytic cycles and active sites communicate with each other.

Task 6) We will first synthesize various H<sub>2</sub>O<sub>2</sub> formation catalysts that are known to be highly active (e.g., Pd, PdAu, and PdP clusters). We hypothesize that by having an electron-withdrawing element (Au, P, Cl) in our Pd catalyst, that rates of olefin and thiophene hydrogenation will be hindered such that H<sub>2</sub>O<sub>2</sub> formation and oxidation will be favored pathways. These experiments will be conducted in semi-batch reactors with controllable H<sub>2</sub> and O<sub>2</sub> pressures at moderate temperatures (313-353 K) and pressures (0.1-1 MPa, with diluent N<sub>2</sub> to avoid forming explosive mixtures). We will create catalysts that give high formation H<sub>2</sub>O<sub>2</sub> selectivities at conditions relevant for alkene epoxidation and thiophene oxidations.

Task 7) We will test the efficacy of the tandem catalysis concept. We will measure the concentrations of alkenes, epoxides, thiophenes and sulfones as functions of time in order to determine rates for each catalytic function and to identify the kinetic “bottlenecks” within bifunctional system and develop hypotheses for methods to improve rates and selectivities for oxidation. In order to determine how the formation of various reactive intermediates affect the relative rates of H<sub>2</sub>O<sub>2</sub> formation and subsequent oxidation, we will combine reaction rate measurements and time-resolved in situ spectroscopy to build understanding of bifunctional catalytic reactions.

### Accomplishments: What we have accomplished:

We have successfully post-synthetically modified commercial zeolite \*BEA to incorporate various transition metals (e.g., Nb, Ti, Ta, Sn, Hf, Zr, Fe, V) into the zeolite (M-BEA). Additionally, we have used ICP-OES, UV-visible spectroscopy, FTIR spectroscopy of chemisorbed-CD<sub>3</sub>CN, and p-XRD to characterize the catalyst metal content, metal-atom isolation, Lewis acidity, and zeolite crystallinity, respectively.

Initial studies focused on the epoxidation of cyclohexene (C<sub>6</sub>H<sub>10</sub>) with H<sub>2</sub>O<sub>2</sub> over Nb-BEA. We made a series of kinetic measurements to study the rates of cyclohexene oxide (C<sub>6</sub>H<sub>10</sub>O) formation and H<sub>2</sub>O<sub>2</sub> decomposition as a function of the reactant (i.e., C<sub>6</sub>H<sub>10</sub>, H<sub>2</sub>O<sub>2</sub>) and product (C<sub>6</sub>H<sub>10</sub>O) concentrations that were consistent with our proposed mechanism for C<sub>6</sub>H<sub>10</sub> epoxidation and H<sub>2</sub>O<sub>2</sub> decomposition. These mechanistic interpretations were corroborated by in situ UV-vis and infrared spectroscopy that were used to identify the activate intermediates for epoxidation. Moreover, measurements of the activation barriers for the two pathways (i.e., epoxidation and H<sub>2</sub>O<sub>2</sub> decomposition) show that the thermodynamics of these competing reaction pathways allow for higher selectivities toward epoxidation at higher temperatures (i.e., epoxidation is favored at higher temperatures). This work has resulted in a manuscript (Journal of Catalysis, 2017, 348, 75-89).

Our work then focused on studying the trends in reactivity among group 4 (Ti, Zr, and Hf) and 5 (Nb and Ta) metal atoms substituted into the zeolite BEA framework, such that each catalyst possessed similar nominal pore sizes and silanol densities so that meaningful trends across the range of catalysts could be observed. We studied the epoxidation of C<sub>6</sub>H<sub>10</sub>, where kinetic measurements show that all M-BEA activate H<sub>2</sub>O<sub>2</sub> through largely identical mechanisms, where the only difference is in the identity of the active intermediate. UV-vis spectra collected in situ, along with the isomeric distribution of the epoxide products from reactions with cis-stilbene, suggest that all M-BEA activate H<sub>2</sub>O<sub>2</sub> to form pools of metal-hydroperoxide (M-OOH) and peroxide (M-( $\eta^2$ -O<sub>2</sub>)) intermediates, where group 4 metals (i.e., Ti, Zr, and Hf) react through M-OOH and group 4 catalysts (i.e., Nb and Ta) epoxidize via M-( $\eta^2$ -O<sub>2</sub>) moieties. Rates of epoxidation (measured at single set of conditions) show that Ti-BEA at 100,000 and 100-times more active and selective, respectively, than Zr-BEA. We showed that activation enthalpies for epoxidation depend linearly on the functional Lewis acid strength of the M-BEA (measured both by the heats of adsorption for deuterated acetonitrile (Fig. 1) and the ligand-to-metal charge transfer (LMCT) band of the active intermediate via UV-vis). Moreover, epoxidation depends more strongly on the Lewis acid strength of the active site than H<sub>2</sub>O<sub>2</sub> decomposition, which suggests that stronger Lewis acids are both more active and selective for epoxidation. This work has resulted in a manuscript (Journal of the American Chemical Society, 2017, 139, 6888-6898).

Next, we began a collaboration with Northwestern University, where our objective was to unify the epoxidation literature between M-BEA and the same metal atoms grafted onto mesoporous SiO<sub>2</sub> (M-SiO<sub>2</sub>). We studied M-BEA and M-SiO<sub>2</sub> (M = Ti, Nb, or Ta) for the epoxidation of styrene (C<sub>8</sub>H<sub>8</sub>) with H<sub>2</sub>O<sub>2</sub>. Kinetic measurements for styrene oxide formation as a function of reactant concentrations showed that the mechanism for epoxidation among these materials are identical. In situ UV-vis spectroscopy showed that all materials irreversibly activate H<sub>2</sub>O<sub>2</sub> to form the same pools of M-OOH and M-( $\eta^2$ -O<sub>2</sub>) intermediates, where both Ti catalysts (Ti-BEA and Ti-SiO<sub>2</sub>) react through Ti-OOH, while Nb and Ta materials epoxidize through M-( $\eta^2$ -O<sub>2</sub>) (as determined by time-resolved in situ UV-vis

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spectroscopy and epoxidation reactions with *cis*-stilbene). Measurement of the activation enthalpies for epoxidation and H<sub>2</sub>O<sub>2</sub> decomposition on both M-BEA and M-SiO<sub>2</sub> show similar trends to those discovered by our group in our J. Am. Chem. Soc. study (see above). Interestingly, we found that the M-BEA materials systematically possess higher rates and selectivities toward epoxidation than their M-SiO<sub>2</sub> counterparts. Moreover, differences between the activation enthalpies for epoxidation between M-BEA and M-SiO<sub>2</sub> catalysts are consistent with the differences in adsorption enthalpy for C<sub>8</sub>H<sub>8</sub> into purely siliceous materials, which suggest that confinement within the micropores of \*BEA are solely responsible for the differences in epoxidation rates, while activation enthalpies for H<sub>2</sub>O<sub>2</sub> decomposition did not change when the type of support (e.g., Ti-BEA versus Ti-SiO<sub>2</sub>) was changed. This work has resulted in a manuscript that is currently in revision with ACS Catalysis.

Finally, our work for the year had changed to study the oxidative desulfurization (ODS; a related chemistry to epoxidations) of hindered thiophenes. Initial studies were investigating the differences in reactivity between different M-BEA (M = Ti, Zr, Nb, and Ta) for the oxidative desulfurization of 2,5-dimethylthiophene (2,5DMT; i.e., our model thiophenic substrate). Kinetic measurements show the dual-catalytic cycle where 2,5DMT undergoes epoxidation through an analogous mechanism to alkene epoxidation to form 2,5-dimethylthiophene oxide (2,5DMTO), which can then be further oxidized to form 2,5-dimethylthiophene sulfone (2,5-DMTO<sub>2</sub>). Interestingly, until ~40% conversion the 2,5DMTO is the primary product (>90% selectivity), presumably because formation of 2,5DMTO<sub>2</sub> is formed via oxidative dearomatization of the thiophene ring. Our work uses in situ UV-vis spectroscopy to implicate sulfoxide (e.g., 2,5DMTO) species as the most abundance surface intermediate at low concentrations (e.g., 1 mM) where we have used dimethylsulfoxide as a proxy for 2,5DMTO (which is not commercially available). Measurements of the activation enthalpies for 2,5DMT ODS show similar trends in reactivity as alkene epoxidation, where Ti is the most active for this chemistry, followed by Nb, Ta, and Zr. This work has resulted in a manuscript that is to be submitted by the end of 2017 to Green Chemistry.

**Training Opportunities:** Work on olefin and thiophene oxidation by M-BEA with H<sub>2</sub>O<sub>2</sub> has allowed for my graduate student, Daniel Bregante, to learn various catalyst- synthesis and characterization techniques. For example, before joining my group, Daniel had no prior experience in synthesizing heterogeneous catalysts or in analyzing rate data and extracting out meaningful information. Since joining, he has developed a procedure for the post-synthetic modification of commercially-available zeolite catalysts, and learning how to characterize them using inductively coupled plasma-optical emission spectroscopy, UV-visible spectroscopy, Infrared spectroscopy, and powder X-ray diffraction. He constructed liquid-phase in situ spectroscopy cells to allow us to use Raman and UV-vis to monitor the formation and consumption of these reactive intermediates on the catalyst surfaces.

Over the period of this project, Daniel and I mentored three undergraduate students - two of which are continuing to work in our lab on this project (Alayna Johnson and Ami Patel). These three undergraduates have learned to run batch reactions and analyze the raw data to extract rates and relate these to mechanistic details of the reaction. They have also been trained in the synthesis of these catalysts and in the use of FTIR and UV-Vis spectroscopy for the characterization of reactive intermediates. These students work closely with Daniel on a daily basis and will be continuing to work with Daniel for the next academic school year and will likely be taught more intricate characterization techniques as they progress.

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**Results Dissemination:** Results obtained during this project have been reported at the following conferences:

- 1) "Direct Synthesis of H<sub>2</sub>O<sub>2</sub> and Epoxidations at Solid-Liquid Interfaces" Gordon Research Conference: Catalysis; New London, New Hampshire, June 12th-June 17th, 2016 (Poster)
- 2) "Direct Synthesis of H<sub>2</sub>O<sub>2</sub> on Pd and Pd-Based Alloy Nanoclusters: Heterolytic and Homolytic Processes at the Liquid-Solid Interface," International Congress on Catalysis, Beijing, China, July, 2016. (Oral Presentation)
- 3) "The Influences of Alloying and Surface Modifications on the Direct Synthesis of H<sub>2</sub>O<sub>2</sub> on Metal Clusters," Heterogeneous Catalysis for Selective Oxidation and Reduction Toward a Green Production, 252nd ACS National Meeting, Philadelphia, PA, August, 2016. (Invited Talk)
- 4) "Mechanisms, Active Intermediates, and Descriptors for Epoxidation Rates and Selectivities on Dispersed Early Transition Metals," 255th ACS National Meeting, Session: I&EC Early Career Fellow: Symposium in Honor of Beata Kilos, New Orleans, LA, 3/2018. (Invited Talk)
- 5) "Understanding Olefin Epoxidation with H<sub>2</sub>O<sub>2</sub> in Transition-Metal Substituted Zeolites," Spring Symposium of the Catalysis Club of Chicago, May 2016, BP Research Center, Naperville, IL.
- 6) "Kinetic and Spectroscopic Evidence for Periodic Trends in Olefin Epoxidation over Group IV and V \*BEA Catalysts," 253rd ACS National Meeting, Session: Elucidation of Mechanism and Kinetics on Surfaces, San Francisco, San Francisco, CA, March, 2017.
- 7) "Periodic Trends in Olefin Epoxidation over Group IV and V Zeolite Catalysts," Spring Symposium of the Catalysis Club of Chicago, BP Research Center, Naperville, IL, May 2017
- 8) "Kinetic and Spectroscopic Evidence for Periodic Trends in Olefin Epoxidation over Group IV and V \*BEA Catalysts," 25th North American Catalysis Society Meeting, Denver, CO, June 2017.
- 9) "Functional Descriptors, Active Intermediates, and the Influence of the Porous Environment for Epoxidations at Lewis Acidic Metal Atoms in Zeolite BEA," American Institute of Chemical Engineering, Annual Meeting, November 2017, Minneapolis, MN.
- 10) "Group IV and V Periodic Trends in Olefin Epoxidation: Effects of Local Environment and Electronic Structure," American Institute of Chemical Engineering, Annual Meeting, November 2017, Minneapolis, MN.
- 11) "The Direct Synthesis of H<sub>2</sub>O<sub>2</sub> and Green Oxidations: Eliminating Needless Chlorine in Industry," University of Delaware, Newark, Department of Chemical Engineering and Catalysis Center for Energy Innovation, Newark, DE, 6/2017.
- 12) "Active Intermediates and Site Requirements for O<sub>2</sub> Activation Reactions and Hydrocarbon Oxidations," SABIC, Corporate Research and Development, Sugar Land, TX, 8/2017.
- 13) "Size and Strength Matter – Requirements for Selective Epoxidations at Lewis Acid Sites within Microporous Catalysts," Rice University, Department of Chemical Engineering, Houston, TX, 10/2017.
- 14) "Catalysis to Eliminate Needless Chlorine in Industry – Direct Synthesis of H<sub>2</sub>O<sub>2</sub> and "Green" Epoxidations," Georgia Tech, School of Chemical and Biomolecular Engineering, Atlanta, GA, 10/2017.
- 15) "The Direct Synthesis of H<sub>2</sub>O<sub>2</sub> and Green Oxidations: Eliminating Needless Chlorine in Industry," ExxonMobil Chemicals, Baytown, TX, 9/2016.
- 16) "The Direct Synthesis of H<sub>2</sub>O<sub>2</sub> and Green Oxidations: Eliminating Needless Chlorine in Industry," University of Houston, Department of Chemical and Biomolecular Engineering, Houston, TX, 9/2016.
- 17) "The Direct Synthesis of H<sub>2</sub>O<sub>2</sub> and Green Oxidations: Eliminating Needless Chlorine in Industry," The Ohio State University, Department of Chemical and Biomolecular Engineering, Columbus, OH, 11/2016.
- 18) "The Direct Synthesis of H<sub>2</sub>O<sub>2</sub> and Green Oxidations: Eliminating Needless Chlorine in Industry," University of Michigan, Department of Chemical Engineering, Ann Arbor, MI, 11/2016.
- 19) "The Direct Synthesis of H<sub>2</sub>O<sub>2</sub> and Green Oxidations: Eliminating Needless Chlorine in Industry," Northwestern University, Department of Chemical and Biological Engineering, Evanston, IL, 12/2016.
- 20) "The Direct Synthesis of H<sub>2</sub>O<sub>2</sub> and Green Oxidations: Eliminating Needless Chlorine in Industry," University of Texas, Austin, Department of Chemical Engineering, Austin, TX, 3/2017.

and ARO support has lead to the following publications:

- 1) Neil M. Wilson, Daniel T. Bregante, Pranjali Priyadarshini, and David W. Flaherty, "Production and Use of H<sub>2</sub>O<sub>2</sub> for Atom-Efficient Functionalization of Hydrocarbons and Small Molecules" Catalysis 2017, 29, 122-212.
- 2) Daniel T. Bregante and David W. Flaherty, "Periodic Trends in Olefin Epoxidation over Group IV and V Framework Substituted Zeolite Catalysts: A Kinetic and Spectroscopic Study" J. Am. Chem. Soc. 2017, 139, 6888-6898.
- 3) Daniel T. Bregante, Pranjali Priyadarshini, and David W. Flaherty, "Kinetic and Spectroscopic Evidence for Reaction Pathways and Intermediates for Olefin Epoxidation on Nb in \*BEA" J. Catal. 2017, 348, 75-89.
- 4) Daniel T. Bregante, Nicholas E. Thornburg, Justin M. Notestein, and David W. Flaherty, "Consequences of Confinement for Alkene Epoxidation with Hydrogen Peroxide on Highly Dispersed Group IV and V Metal Oxide

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Catalysts" in review, ACS Catal.

**Honors and Awards:** Nothing to Report

**Protocol Activity Status:**

**Technology Transfer:** Nothing to Report

**PARTICIPANTS:**

**Participant Type:** PD/PI

**Participant:** David Flaherty

**Person Months Worked:** 1.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Graduate Student (research assistant)

**Participant:** Pranjali Priyadarshini

**Person Months Worked:** 5.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Graduate Student (research assistant)

**Participant:** Daniel Bregante

**Person Months Worked:** 7.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Undergraduate Student

**Participant:** Katherine Nagode

**Person Months Worked:** 3.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

**Participant Type:** Undergraduate Student

**Participant:** Alayna Johnson

**Person Months Worked:** 3.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

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**Participant Type:** Undergraduate Student

**Participant:** Ami Patel

**Person Months Worked:** 3.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

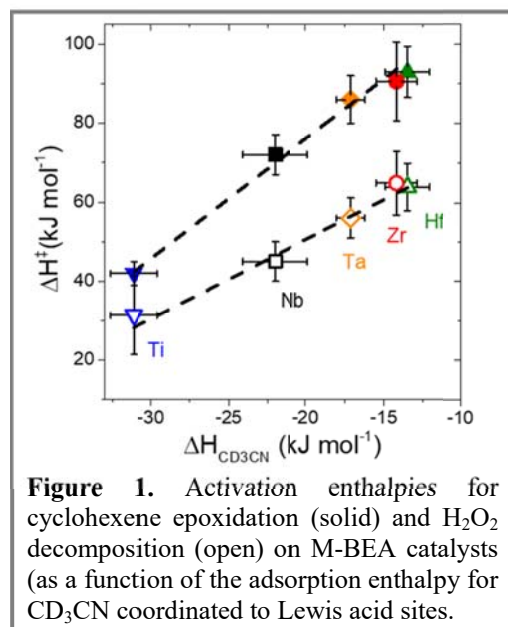
Other Collaborators:

**What we have accomplished:**

We have successfully post-synthetically modified commercial zeolite \*BEA to incorporate various transition metals (e.g., Nb, Ti, Ta, Sn, Hf, Zr, Fe, V) into the zeolite (M-BEA). Additionally, we have used ICP-OES, UV-visible spectroscopy, FTIR spectroscopy of chemisorbed- $\text{CD}_3\text{CN}$ , and p-XRD to characterize the catalyst metal content, metal-atom isolation, Lewis acidity, and zeolite crystallinity, respectively.

Initial studies focused on the epoxidation of cyclohexene ( $\text{C}_6\text{H}_{10}$ ) with  $\text{H}_2\text{O}_2$  over Nb-BEA. We made a series of kinetic measurements to study the rates of cyclohexene oxide ( $\text{C}_6\text{H}_{10}\text{O}$ ) formation and  $\text{H}_2\text{O}_2$  decomposition as a function of the reactant (i.e.,  $\text{C}_6\text{H}_{10}$ ,  $\text{H}_2\text{O}_2$ ) and product ( $\text{C}_6\text{H}_{10}\text{O}$ ) concentrations that were consistent with our proposed mechanism for  $\text{C}_6\text{H}_{10}$  epoxidation and  $\text{H}_2\text{O}_2$  decomposition. These mechanistic interpretations were corroborated by *in situ* UV-vis and infrared spectroscopy that were used to identify the activate intermediates for epoxidation. Moreover, measurements of the activation barriers for the two pathways (i.e., epoxidation and  $\text{H}_2\text{O}_2$  decomposition) show that the thermodynamics of these competing reaction pathways allow for higher selectivities toward epoxidation at higher temperatures (i.e., epoxidation is favored at higher temperatures). This work has resulted in a manuscript (*Journal of Catalysis*, **2017**, 348, 75-89).

Our work then focused on studying the trends in reactivity among group 4 (Ti, Zr, and Hf) and 5 (Nb and Ta) metal atoms substituted into the zeolite BEA framework, such that each catalyst possessed similar nominal pore sizes and silanol densities so that meaningful trends across the range of catalysts could be observed. We studied the epoxidation of  $\text{C}_6\text{H}_{10}$ , where kinetic measurements show that all M-BEA activate  $\text{H}_2\text{O}_2$  through largely identical mechanisms, where the only difference is in the identity of the active intermediate. UV-vis spectra collected *in situ*, along with the isomeric distribution of the epoxide products from reactions with *cis*-stilbene, suggest that all M-BEA activate  $\text{H}_2\text{O}_2$  to form pools of metal-hydroperoxide (M-OOH) and peroxide (M-( $\eta^2$ - $\text{O}_2$ )) intermediates, where group 4 metals (i.e., Ti, Zr, and Hf) react through M-OOH and group 4 catalysts (i.e., Nb and Ta) epoxidize via M-( $\eta^2$ - $\text{O}_2$ ) moieties. Rates of epoxidation (measured at single set of conditions) show that Ti-BEA at 100,000 and 100-times more active and selective, respectively, than Zr-BEA. We showed that activation enthalpies for epoxidation depend linearly on the functional Lewis acid strength of the M-BEA (measured both by the heats of adsorption for deuterated acetonitrile (Fig. 1) and the





ligand-to-metal charge transfer (LMCT) band of the active intermediate *via* UV-vis). Moreover, epoxidation depends more strongly on the Lewis acid strength of the active site than H<sub>2</sub>O<sub>2</sub> decomposition, which suggests that stronger Lewis acids are both more active and selective for epoxidation. This work has resulted in a manuscript (*Journal of the American Chemical Society*, **2017**, *139*, 6888-6898).

Next, we began a collaboration with Northwestern University, where our objective was to unify the epoxidation literature between M-BEA and the same metal atoms grafted onto mesoporous SiO<sub>2</sub> (M-SiO<sub>2</sub>). We studied M-BEA and M-SiO<sub>2</sub> (M = Ti, Nb, or Ta) for the epoxidation of styrene (C<sub>8</sub>H<sub>8</sub>) with H<sub>2</sub>O<sub>2</sub>. Kinetic measurements for styrene oxide formation as a function of reactant concentrations showed that the mechanism for epoxidation among these materials are identical. *In situ* UV-vis spectroscopy showed that all materials irreversibly activate H<sub>2</sub>O<sub>2</sub> to form the same pools of M-OOH and M-( $\eta^2$ -O<sub>2</sub>) intermediates, where both Ti catalysts (Ti-BEA and Ti-SiO<sub>2</sub>) react through Ti-OOH, while Nb and Ta materials epoxidize through M-( $\eta^2$ -O<sub>2</sub>) (as determined by time-resolved *in situ* UV-vis spectroscopy and epoxidation reactions with *cis*-stilbene). Measurement of the activation enthalpies for epoxidation and H<sub>2</sub>O<sub>2</sub> decomposition on both M-BEA and M-SiO<sub>2</sub> show similar trends to those discovered by our group in our *J. Am. Chem. Soc.* study (see above). Interestingly, we found that the M-BEA materials systematically possess higher rates and selectivities toward epoxidation than their M-SiO<sub>2</sub> counterparts. Moreover, differences between the activation enthalpies for epoxidation between M-BEA and M-SiO<sub>2</sub> catalysts are consistent with the differences in adsorption enthalpy for C<sub>8</sub>H<sub>8</sub> into purely siliceous materials, which suggest that confinement within the micropores of \*BEA are solely responsible for the differences in epoxidation rates, while activation enthalpies for H<sub>2</sub>O<sub>2</sub> decomposition did not change when the type of support (e.g., Ti-BEA versus Ti-SiO<sub>2</sub>) was changed. This work has resulted in a manuscript that is currently in revision with *ACS Catalysis*.

Finally, our work for the year had changed to study the oxidative desulfurization (ODS; a related chemistry to epoxidations) of hindered thiophenes. Initial studies were investigating the differences in reactivity between different M-BEA (M = Ti, Zr, Nb, and Ta) for the oxidative desulfurization of 2,5-dimethylthiophene (2,5DMT; i.e., our model thiophenic substrate). Kinetic measurements show the dual-catalytic cycle where 2,5DMT undergoes epoxidation through an analogous mechanism to alkene epoxidation to form 2,5-dimethylthiophene oxide (2,5DMTO), which can then be further oxidized to form 2,5-dimethylthiophene sulfone (2,5-DMTO<sub>2</sub>). Interestingly, until ~40% conversion the 2,5DMTO is the primary product (>90% selectivity), presumably because formation of 2,5DMTO<sub>2</sub> is formed via oxidative dearomatization of the thiophene ring. Our work uses *in situ* UV-vis spectroscopy to implicate sulfoxide (e.g., 2,5DMTO) species as the most abundance surface intermediate at low concentrations (e.g., 1 mM) where we have used dimethylsulfoxide as a proxy for 2,5DMTO (which is not commercially available). Measurements of the activation enthalpies for 2,5DMT ODS show similar trends in reactivity as alkene epoxidation, where Ti is the most active for this chemistry,

followed by Nb, Ta, and Zr. This work has resulted in a manuscript that is to be submitted by the end of 2017 to *Green Chemistry*.